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Physical properties of normal two-electron systems considering correlation

Arijit Ghoshal, Sabyasachi Kar and Puspajit Mandal*
Department of Mathematics, Visva-Bharati University, Santiniketan-731 235, West Bengal, India

Abstract : A number of correlated wave functions having two types of correlation for the ground state of helium iso-electronic systems, have been proposed in the following forms (a.u.) :

(i) $\Psi = \sum c_i r_1^{l_i} r_2^{m_i} r_{12}^{n_i} \exp[-(Ar_1 + Br_2 + \mu_i r_{12})] + (1 \Leftrightarrow 2)$, and

(ii) $\Psi = \sum c_i r_1^{l_i} r_2^{m_i} r_{12}^{n_i} \exp[-A(r_1 + r_2)]/(a + br_{12})^{m_0} + (1 \Leftrightarrow 2)$, where $l + m + n < \omega$ (integer), and $m_0 = \frac{1}{2}, \frac{3}{2}...$

We have used Monte- Carlo method to optimize the sets of the exponential correlation parameter μ_i along with the other nonlinear variation parameters A, B to determine quite accurate eigen energies and other physical properties within the framework of the Rayleigh-Ritz variational principle.

The corresponding eigen energies ϵ (a.u.) and other observable quantities, such as, magnetic susceptibility χ (cm^3) are in good agreement with the accurate results available in the literature. The wave functions may be of use in atomic collision problems where correlations between the electrons play an important role.

Keywords : Normal two-electron systems, eigenenergy, exponential correlation, inverse correlation, Monte-Carlo optimization.

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1. Introduction

The best way to understand the nature of interectronic repulsion, globally known as correlation [1], is to study the wavefunctions of two-electron atoms and ions. This two-electron bound system is the simplest of all quantum mechanical systems in which such a correlation plays a vital role and thus it has been drawing serious attention of many workers in the field of atomic and molecular physics since the early days of quantum mechanics. Till this date, many workers have solved this problem to an amazing accuracy [1–9] using variational principles and otherwise with various degree of sophistication. Still this problem remains a live field because (i) the essentially 'exact' wavefunctions (Pekeris-246 terms [2], Drake and Yan-1262 terms[3], Korobov-2200 terms [4] *etc.*) contain a large number of terms as well as nonlinear variational parameters in its expansion, so it is difficult to extract informations easily regarding the physical properties of the systems; (ii) it is very difficult to implement such wavefunctions in further applications of atomic structure and atomic collisions in which correlation is one of the important factors. So, it is desirable to have simple analytic wavefunctions which can take into account the essential physical features of the exact wavefunction. There are several efforts in this direction [10–14], we shall not discuss them here. Rather, we shall first analyse the properties of an essentially exact wavefunction, and, incorporating them judiciously, shall construct several analytic wavefunctions within the framework of Rayleigh-Ritz variational principle.

The nonrelativistic Schrödinger wave equation for normal two-electron systems is given by

$$(H - E)\ \Psi(r_1, r_2, r_{12}) = 0, \qquad (1)$$

E is the ground state energy of the system, r_1, r_2 are the coordinates of the electrons relative to the nucleus while r_{12} is the relative coordinates of the electron 1 with respect to electron 2. Here, H denotes the Hamiltonian of

*Corresponding Author

two-electron systems and is described (neglecting the motion of the nucleus) in atomic units (a.u.) by :

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \tag{2}$$

$$= H_1 + H_2 + H_{12} + H'_{12} \tag{3}$$

with

$$H_i = -\frac{1}{2}\left(\frac{\partial^2}{\partial r_i^2} + \frac{2}{r_i}\frac{\partial}{\partial r_i}\right) - \frac{Z}{r_i},$$

$$H_{12} = -\left(\frac{\partial^2}{\partial r_{12}^2} + \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}}\right) + \frac{1}{r_{12}}$$

$$H'_{12} = -\frac{1}{2}\left(\cos(\vartheta_1)\frac{\partial}{\partial r_1} + \cos(\vartheta_2)\frac{\partial}{\partial r_2}\right)\frac{\partial}{\partial r_{12}}, \tag{4}$$

where ϑ_i is the angle made at the i-th electron by r_i and r_{12}, i = 1, 2, Z being the nuclear change of the systems.

It is to be metioned that the operators H_i and H_{12} have a singularity for $r_i = 0$ and $r_{12} = 0$, respectively, while H'_{12} has a singularity for the simultaneous value of $r_1 = r_2 = r_{12} = 0$, since the values of $\cos\vartheta_i$ depend on how the triangle joining r_1, r_2 and r_{12} is contracted to a point.

We write our wavefunction as the product of three functions as :

$$\Psi(r_1, r_2, r_{12}) = \phi_1(r_1).\phi_2(r_2).\chi(r_{12}), \tag{5}$$

where ϕ_1 is a function of r_1 alone, ϕ_2 is a function of r_2 alone and χ, called the correlation function, is a function of r_{12} alone. We now consider the behaviour of exact Ψ for different boundary conditions.

(i) When one of the electrons is very near the nucleus, i.e. say $r_1 \to 0$, the terms $-\frac{1}{2}\nabla_1^2$ and $-\frac{Z}{r_1}$ will dominate the Hamiltonian, and from this, one can show that [13]

$$\Psi \to g(r_2) \text{ as } r_1 \to 0.$$

Similarly,

$$\Psi \to g(r_1) \text{ as } r_2 \to 0, \tag{6}$$

where g is a function of r_1 alone in one case and a function of r_2 in the other. These equations are immediate consequence of Kato's theorem on electron-nucleus orbital cusp [15]

$$\lim_{r_i \to 0}\left(\frac{\partial \Psi}{\partial r_i}\right)_{av} = -Z\Psi(r_i = 0). \tag{7}$$

(ii) When one of the electrons is far away from the nucleus, say $r_1 \to \infty$, this electron will be in the Coulomb field shielded by the other and its wavefunction has a long range asymptotic form [16–18]. Consequently,

$$\Psi \to \frac{}{\sqrt{4\pi}} g_1(r_2) r^{\frac{(Z-1)}{\beta-1}} e^{-\beta r_1} \text{ as } r_1 \tag{8}$$

where $\beta = \sqrt{2E_1}$, E_1 is the first ionization energy, and A is the normalisation constant. Moreover, the wavefunction of the residue systems will be hydrogen-like with nuclear charge Z, *i.e.*

$$g_1(r_2) = \frac{Z^{3/2}}{\sqrt{\pi}} e^{-Zr_2}$$

Thus,

$$\Psi \to \frac{Z^{3/2}}{2\pi} e^{-Zr_2} r_1^{\frac{(Z-1)}{\beta-1}} e^{-\beta r_1} \text{ as } r_1$$

$$\Psi \to \frac{Z^{3/2}}{2\pi} e^{-Zr_1} r_2^{\frac{(Z-1)}{\beta-1}} e^{-\beta r_2} \text{ as } r_2 \tag{9}$$

where r_i (i = 1, 2) is the coordinate of the either electron and av in eq. (7) denotes the spherical averaging.

(iii) When the electrons are close to each other, i.e. $r_{12} \to 0$ in comparison with r_1 and r_2, the term $\frac{1}{r_{12}}$ will lead the potential. Kato [15] showed that

$$\lim_{r_{12} \to 0}\left(\frac{\partial \Psi}{\partial r_{12}}\right)_{av} = \frac{1}{2}\Psi(r_{12} = 0), \tag{10}$$

where the factor $\frac{1}{2}$ is due to the reduced mass of electrons. This condition is referred to as the cusp conditon. It is, of course, a measure of goodness of the wavefunction. From this condition, it follows that

$$\Psi \to \phi_1(r_1)\phi_2(r_2)\left[1 + \frac{1}{2}r_{12} + \cdots\right] \text{ as } r_{12} \to 0. \tag{11}$$

Another consequence of eq. (11) is that the correlation function χ should be in the form :

$$\chi(r_{12}) = 1 + \frac{r_{12}}{2} + \cdots \tag{12}$$

Eq. (12) demands that $\chi(r_{12}) \to 1$ as $r_{12} \to 0$.

(iv) When both the electrons are very close to the origin, i.e. $r_1 \to 0$ and $r_2 \to 0$, Ψ should remain finite.

(v) When both the electrons are far away from the nucleus, i.e. $r_1 \to \infty$ and $r_2 \to \infty$, r_{12} may or may not be finite, the wavefunction Ψ should vanish. As the bound system is confined in a finite volume in space, there arises no possibility of allowing $r_{12} \to \infty$ without making $r_1, r_2 \to \infty$ at the same time, which would always make $\psi \to 0$ in the limit.

Besides the above properties describing the spatial behaviour of electrons in configuration space, an exact Ψ should also satisfy some well known global properties such as the Virial theorem. This theorem states that the ratio of the average value of the potential energy to the average value of the kinetic energy is equal to –2. Further, that the expectation of the Hamiltonian should be minimum is another important proparty to be satisfied by ψ.

2. Theory

In view of the above, we propose a few simple analytic, correlated wavefunction for the normal two-electron systems broadly falling into two categories, namely, wavefunction having exponential correlation $\left(e^{-\mu_i r_{12}}\right)$ and wavefunctions having inverse correlation $\left(\frac{1}{a+br_{12}}\right)$, in the form :

$$\Psi = \phi_1(r_1)\phi_2(r_2)\chi(r_{12})$$

and expand $\phi_i(r_i)$ $(i = 1, 2)$ and $\chi(r_{12})$ respectively in terms of r_i and r_{12},

$$\phi_i(r_i) = \sum c_i e^{-A_i r_i} r_i^{l_i}, \tag{13}$$

$$\chi(r_{12}) = \sum c_i e^{-\mu_i r_{12}} r_{12}^{n_i} \tag{14}$$

$$\chi(r_{12}) = \sum c_i e^{-\mu_i r_{12}} \frac{1}{(a+br_{12})^{m_0}}, \tag{15}$$

so that the wavefunction with two types of correlation functions is formally expressed as

$$\text{(A)}\Psi(r_1, r_2, r_{12}) = \sum_{i=0}^{N} c_i e^{-(Ar_1+Br_2+\mu_i r_{12})} r_1^{l_i} r_2^{m_i} r_{12}^{n_i} + (r_1 \Leftrightarrow r_2), \tag{16}$$

$$\text{(B)}\ \Psi(r_1, r_2, r_{12}) = e^{-A(r_1+r_2)} \sum_{i=0}^{N} c_i r_1^{l_i} r_2^{m_i} r_{12}^{n_i} + (r_1 \Leftrightarrow r_2) \frac{1}{(a+br_{12})^{m_0}} \tag{17}$$

where $l_i + m_i + n_i \le \omega$, a positive integer, A, B, μ_i, a, b are nonlinear variational parameters and $m_0 = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$

Exponential correlation functions :

We have considered the following six small basis-set wavefunctions with exponential correlation,

$$\text{(I)}\Psi = \phi(r_1)\varphi(r_2)\chi r_{12} \tag{18}$$

$$= \frac{N}{\pi}\exp[-(Ar_1 + Br_2) + (1 \Leftrightarrow 2)][1 + 0.5r_{12}\exp(-\mu r_{12})], \tag{19}$$

$$\text{(II)}\Psi = \frac{N}{\pi}\exp[-(Ar_1 + Br_2) + (1 \Leftrightarrow 2)] \left[1 + (0.5r_{12} + c_2 r_1 r_{12}^2)\exp(-\mu r_{12})\right], \tag{20}$$

$$\text{(III)}\Psi = \frac{N}{\pi}\exp[-(Ar_1 + Br_2) + (1 \Leftrightarrow 2)] \left[1 + 0.5r_{12}\exp(-\mu_1 r_{12}) + c_2 r_1 r_{12}^2 \exp(-\mu_2 r_{12})\right], \tag{21}$$

$$\text{(IV)}\Psi = \frac{N}{\pi}\exp[-(Ar_1 + Br_2) + (1 \Leftrightarrow 2)] \left[1 + (0.5r_{12} + c_2 r_1 r_2 r_{12}^2)\exp(-\mu r_{12})\right], \tag{22}$$

$$\text{(V)}\Psi = \frac{N}{\pi}\exp[-(Ar_1 + Br_2) + (1 \Leftrightarrow 2)] \left[1 + 0.5r_{12}\exp(-\mu_1 r_{12}) + c_2 r_1 r_2 r_{12}^2 \exp(-\mu_2 r_{12})\right], \tag{23}$$

$$\text{(VI)}\Psi = \frac{N}{\pi}\exp[-(Ar_1 + Br_2) + (1 \Leftrightarrow 2)] \left[1 + 0.5r_{12}\exp(-\mu_1 r_{12}) + c_2 r_1 \exp(-\mu_2 r_{12}) \right. \tag{24}$$

$$\left. + c_3 r_2 \exp(-\mu_3 r_{12}) + c_4 r_1 r_{12}\exp(-\mu_4 r_{12}) + c_5 r_2 r_{12}\exp(-\mu_5 r_{12}) + c_6 r_1 r_2 \exp(-\mu_6 r_{12})\right], \tag{25}$$

The above six wavefunctions having major part of the correlation in their exponent satisfy all the local conditions (i-v) listed above except that these wavefunctions are able to retain 92% of the exact orbital cusp value. Thus, this choice of the wavefunction seems to have a sound physical foundation.

Inverse correlation functions :

The inverse-type correlation has been used in two types of wavefunctions. The first type having only two terms in its expansion is in the form :

$$\text{(VII)}\Psi(r_1,r_2) = N\frac{e^{-(Z+p)r_1-(Z-q)r_2}}{(a+br_{12})^{\frac{1}{2}}}[c_0+c_1r_{12}](1\Leftrightarrow 2), \quad (26)$$

while the second type is of general nature and is given by

$$\text{(VIII)}\ \Psi(r_1,r_2,r_{12}) = N\frac{\exp[-A(r_1+r_2)]}{(a+br_{12})^{\frac{1}{2}}}$$

$$[c_0+c_1r_{12}+c_2r_1+c_3r_1r_2+c_4r_1r_{12}$$

$$+c_5r_{12}^2+c_6r_1^2+c_7r_1^2r_2+c_8r_1r_{12}^2$$

$$+r_1r_2(c_9r_{12}+c_{10}r_{12}^2) \quad (27)$$

$$+r_1\Leftrightarrow r_2], \quad (28)$$

with only two nonlinear variational parameters, A, b, where we set $a = 1$.

These two wavefunctions inspite of the fact that they include infinite order correlation through the inverse of half powers, do not seem to satisfy the two main features of the exact wavefunctions listed above, namely, the condition describing the orbital cusp and the condition showing the correlation cusp. This is due to the fact that we have somehow relaxed these conditions to some extent to make the eigen energy the most minimum. But, interestingly, we have seen that when the wavefunction VIII has been constrained to satisfy the exact correlation cusp condition it yields an energy higher than the previously minimized energy of the unconstrained systems. It is thus plausible to assume that if one extends the correlation function, keeping the correlation cusp condition always satisfied, by incorporating powers of r_{12}, the saturation point $\left(\inf\frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle}\right)$ will be reached ultimately when this correlation function will fill up the entire configuration space. Conversely, if one goes on minimizing the expression $\frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle}$ on extending the correlation function, by including more and more powers of r_{12}, one will achieve the exact correlation cusp condition as well as the most minimum energy when the correlation function will spread out in the entire configuration space.

Determination of eigen energy :

The standard eigenvalue problem to be solved in this case, according to Rayleigh-Ritz variational principle, is of the form :

$$\boldsymbol{Hc} = \epsilon\boldsymbol{Sc}, \quad (29)$$

where $\boldsymbol{H}$, $\boldsymbol{S}$ are respectively the Hamiltonian and overlap matrices with the vectors of expansion $\boldsymbol{c}$ and eigenvalues, ϵ. All matrix elements in our calculations are obtained analytically by a general procedure, save an overall integration for the Laplace transform :

$$(a+br)^{-m_0} = [\Gamma(m_0)]^{-1}\int_0^\infty \exp[-(a+br)t]\,t^{m_0-1}dt$$

for the inverse type correlation functions. The eigenvalue equation [eq. (29)] has been solved by two different methods after transforming the general equation to the standard form by multiplying both sides with S^{-1},

$$\boldsymbol{Ac} = \epsilon\boldsymbol{c},\ \boldsymbol{A} = \boldsymbol{S}^{-1}\boldsymbol{H}. \quad (30)$$

The results are then checked by a third method.

The nonlinear variational parameters, A, B, b, μ_i, have been optimized by the Monte-Carlo technique [19].

It deserves to be mentioned here that all our calculations are stable and we have tested the accuracy as well as smooth pattern of convergence for all the reported wavefunctions.

3. Results and discussion

Results are reported for the ground state of the two-electron systems for $Z = 1$ through $Z = 10$. Table 1 displays the energy of the systems in a.u. where as Tables 2–9 display the physical observables such as correlation cusp, orbital cusp, various expectation values and magnetic susceptibility *etc.* From Table 1, it is clear that with the inclusion of terms one by one in the correlation function of the wavefunction I, the eigen energies for wavefunctions II to VI having exponential correlation decrease

Table 1. The eigenenrgies $-\epsilon$ (a.u.) corresponding to the wavefunctions I to VIII for the two-electron systems.

	H^-	He	Li^+	Be^{2+}	B^{3+}
Z	1	2	3	4	5
$-\epsilon(1)$	0.525722	2.901102	7.276886	13.652231	22.027446
$-\epsilon(2)$	0.526160	2.901608	7.277889	13.653694	22.029174
$-\epsilon(3)$	0.526195	2.901850	7.278204	13.653914	22.029298
$-\epsilon(4)$	0.526543	2.902969	7.279063	13.654637	22.029982
$-\epsilon(5)$	0.526894	2.903150	7.278987	13.654386	22.029526
$-\epsilon(6)$	0.527100	2.903660	7.279700	13.655128	22.030224
$-\epsilon(7)$	0.526027	2.901993	7.277917	13.653283	22.028446
$-\epsilon(8)$	0.52682	2.90370	7.27986	13.65548	22.03086
	C^{4+}	N^{5+}	O^{6+}	F^{7+}	Ne^{8+}
Z	6	7	8	9	10
$-\epsilon(1)$	32.402668	44.777809	59.152852	75.527852	93.903054
$-\epsilon(2)$	32.404505	44.779784	59.155055	75.530175	93.905282
$-\epsilon(3)$	32.404422	44.779677	59.154816	75.530044	93.905162
$-\epsilon(4)$	32.405231	44.780431	59.155566	75.530664	93.905757
$-\epsilon(5)$	32.404623	44.779795	59.154932	75.530032	93.9020313
$-\epsilon(6)$	32.405445	44.780557	59.155388	75.530240	93.906201
$-\epsilon(7)$	32.403528	44.778570	59.153592	75.528604	93.903609
$-\epsilon(8)$	32.40612	44.78130	59.15644	75.53155	93.90664

Table 2. The correlation cusps $\eta = \left| \frac{1}{\chi} \frac{\partial \chi}{\partial r_{12}} \right)_{r_{12} \to 0}$ corresponding to the wavefunctions I to VIII for the two-electron systems.

	H^-	He	Li^+	Be^{2+}	B^{3+}
Z	1	2	3	4	5
$\eta(1)$	0.5	0.5	0.5	0.5	0.5
$\eta(2)$	0.5	0.5	0.5	0.5	0.5
$\eta(3)$	0.5	0.5	0.5	0.5	0.5
$\eta(4)$	0.5	0.5	0.5	0.5	0.5
$\eta(5)$	0.5	0.5	0.5	0.5	0.5
$\eta(6)$	0.5	0.5	0.5	0.5	0.5
$\eta(7)$	0.410	0.393	0.338	0.313	0.298
$\eta(8)$	0.396	0.379	0.403	0.419	0.426
	C^{4+}	N^{5+}	O^{6+}	F^{7+}	Ne^{8+}
Z	6	7	8	9	10
$\eta(1)$	0.5	0.5	0.5	0.5	0.5
$\eta(2)$	0.5	0.5	0.5	0.5	0.5
$\eta(3)$	0.5	0.5	0.5	0.5	0.5
$\eta(4)$	0.5	0.5	0.5	0.5	0.5
$\eta(5)$	0.5	0.5	0.5	0.5	0.5
$\eta(6)$	0.5	0.5	0.5	0.5	0.5
$\eta(7)$	0.289	0.283	0.277	0.274	0.271
$\eta(8)$	0.432	0.434	0.437	0.438	0.450

Table 3. The orbital cusps $\varsigma = \left| \frac{1}{\phi} \frac{\partial \phi}{\partial r_2} \right)_{r_2 \to 0}$ corresponding to the wavefunctions I to VIII for the two-electron systems.

	H^-	He	Li^+	Be^{2+}	B^{3+}
Z	1	2	3	4	5
$\varsigma(1)$	0.7671	1.8088	2.816	3.8286	4.8233
$\varsigma(2)$	0.78065	1.819	2.8448	3.84775	4.84775
$\varsigma(3)$	0.79200	1.81825	2.84005	3.8482	4.8544
$\varsigma(4)$	0.81600	1.8345	2.84295	3.8428	4.8458
$\varsigma(5)$	0.7995	1.847	2.8375	3.8517	4.85275
$\varsigma(6)$	0.7635	1.900	2.766	3.748	4.7605
$\varsigma(7)$	0.76575	1.811	2.8251	3.831	4.8342
$\varsigma(8)$	0.87264	1.921	2.92999	3.93477	4.93645
	C^{4+}	N^{5+}	O^{6+}	F^{7+}	Ne^{8+}
Z	6	7	8	9	10
$\varsigma(1)$	5.81465	6.82835	7.83085	8.8329	9.8255
$\varsigma(2)$	5.8481	6.8505	7.85375	8.8509	9.8521
$\varsigma(3)$	5.86	6.8585	7.8577	8.8531	9.85685
$\varsigma(4)$	5.848	6.84765	7.8465	8.845	9.8464
$\varsigma(5)$	5.85215	6.8506	7.8496	8.84915	9.8745
$\varsigma(6)$	5.7685	6.774	7.7975	8.813	9.722
$\varsigma(7)$	5.83575	6.8366	7.83715	8.838	9.83875
$\varsigma(8)$	5.93671	6.93650	7.93643	8.93564	9.93632

Table 4. The expectation values $p_1 = \langle r_1 \rangle$ for the distance of an electron from the nucleus corresponding to the wavefunctions I to VIII for the two-electron systems.

	H^-	He	Li^+	Be^2	B^{3+}
Z	1	2	3	4	5
$p_1(1)$	2.591060	0.920417	0.569122	0.411622	0.323221
$p_1(2)$	2.634870	0.926556	0.570856	0.413318	0.323975
$p_1(3)$	2.632371	0.925236	0.571713	0.413195	0.323976
$p_1(4)$	2.616724	0.929643	0.572781	0.414130	0.324401
$p_1(5)$	2.621963	0.929757	0.572822	0.413500	0.323841
$p_1(6)$	2.626006	0.929590	0.573163	0.414149	0.324199
$p_1(7)$	2.612900	0.924521	0.571176	0.413619	0.324226
$p_1(8)$	2.56962	0.92938	0.57285	0.41431	0.32457
	C^{4+}	N^{5+}	O^{6+}	F^{7+}	Ne^{8+}
Z	6	7	8	9	10
$p_1(1)$	0.266151	0.225734	0.196152	0.173434	0.155563
$p_1(2)$	0.266402	0.226226	0.196613	0.173813	0.155759
$p_1(3)$	0.266056	0.226125	0.196536	0.173838	0.155734
$p_1(4)$	0.266697	0.226456	0.196734	0.173964	0.155878
$p_1(5)$	0.266282	0.226100	0.196481	0.173718	0.155692
$p_1(6)$	0.266670	0.226466	0.196590	0.173823	0.155882
$p_1(7)$	0.266600	0.226369	0.196693	0.173892	0.155828
$P_1(8)$	0.26680	0.22650	0.19677	0.17395	0.15586

Table 5. The expectation values $p_2 = \left\langle \frac{1}{r_2} \right\rangle$ for the reciprocal of the distance of an electron from the nucleus corresponding to the wavefunctions I to VIII for the two-electron systems.

	H^-	He	Li^+	Be^{2+}	B^{3+}
	1	2	3	4	5
$p_2(1)$	0.683494	1.688366	2.687790	3.691359	4.684878
$p_2(2)$	0.683270	1.687942	2.687631	3.687495	4.687661
$p_2(3)$	0.684709	1.687600	2.687762	3.690476	4.690081
$p_2(4)$	0.685499	1.688178	2.688070	3.687073	4.687127
$p_2(5)$	0.684858	1.688218	2.684281	3.689669	4.690165
$p_2(6)$	0.684829	1.688310	2.687128	3.686094	4.688139
$p_2(7)$	0.684196	1.687863	2.687699	3.687674	4.687896
$p_2(8)$	0.68756	1.68830	2.68789	3.68773	4.68765
	C^{4+}	N^{5+}	O^{6+}	F^{7+}	Ne^{8+}
	6	7	8	9	10
$p_2(1)$	5.684806	6.689465	7.689988	8.690118	9.687364
$p_2(2)$	5.688120	6.688267	7.688047	8.688060	9.688178
$p_2(3)$	5.694395	6.690890	7.699187	8.686186	9.688992
$p_2(4)$	5.687188	6.686944	7.687899	8.686563	9.687060
$p_2(5)$	5.689711	6.690109	7.689842	8.689762	9.686548
$p_2(6)$	5.686255	6.684214	7.688880	8.687908	9.687063
$p_2(7)$	5.687629	6.687346	7.687263	8.687582	9.687914
$p_2(8)$	5.68761	6.68758	7.68756	8.68754	9.68761

Table 6. The expectatation values $p_3 = \left\langle \frac{1}{r_{12}} \right\rangle$ for the reciprocal of the inter-electronic distance corresponding tyo the wavefunctions I to VIII for the two-electron systems.

	H^-	He	Li+	Be^{2+}	B^{3+}
	1	2	3	4	5
$p_3(1)$	0.314517	0.945091	1.565605	2.190447	2.811215
$p_3(2)$	0.315206	0.941982	1.564764	2.188513	2.812631
$p_3(3)$	0.316329	0.946774	1.569492	2.195244	2.818048
$p_3(4)$	0.317816	0.946148	1.566971	2.189472	2.812916
$p_3(5)$	0.315259	0.945397	1.565343	2.190049	2.814218
$p_3(6)$	0.314694	0.945698	1.566602	2.188524	2.811997
$p_3(7)$	0.315925	0.948835	1.570923	2.194392	2.818590
$p_3(8)$	0.32133	0.94586	1.56770	2.19094	2.81481
	C^{4+}	N^{5+}	O^{6+}	F^{7+}	Ne^{8+}
	6	7	8	9	10
$p_3(1)$	3.433721	4.061220	4.686381	5.311468	5.932902
$p_3(2)$	3.437295	4.062041	4.687022	5.312790	5.937314
$p_3(3)$	3.445910	4.067245	4.690239	5.313355	5.939624
$p_3(4)$	3.436910	4.061231	4.686256	5.309829	5.935072
$p_3(5)$	3.437983	4.063204	4.687549	5.312230	5.919913
$p_3(6)$	3.434793	4.058880	4.684402	5.306997	5.936607
$p_3(7)$	3.443273	4.068115	4.692927	5.317825	5.942769
$p_3(8)$	3.43905	4.06350	4.68809	5.31276	5.93754

Table 7. The expectation values $p_4 = \left\langle r_1^2 + r_2^2 \right\rangle$ for the sum of the square of the distaces of the two electrons from the nucleus corresponding to the wavefunctions I to VIII for the two-electron systems.

	H^-	He	Li^+	Be^{2+}	B^{3+}
	1	2	3	4	5
$p_4(1)$	20.423787	2.324575	0.877216	0.456298	0.280575
$p_4(2)$	21.590203	2.375509	0.886481	0.461983	0.282945
$p_4(3)$	21.626329	2.369447	0.891662	0.462270	0.283267
$p_4(4)$	21.245448	2.398645	0.895159	0.464461	0.283938
$p_4(5)$	21.215434	2.396202	0.894037	0.462655	0.282655
$p_4(6)$	21.279129	2.387865	0.894932	0.463888	0.283239
$p_4(7)$	21.033047	2.358151	0.887381	0.462796	0.283527
$p_4(8)$	19.93216	2.38554	0.89278	0.46414	0.28392
	C^{4+}	N^{5+}	O^{6+}	F^{7+}	Ne^{8+}
	6	7	8	9	10
$p_4(1)$	0.190178	0.136566	0.103028	0.080491	0.064761
$p_4(2)$	0.190945	0.137515	0.103781	0.080136	0.065035
$p_4(3)$	0.190499	0.137441	0.103711	0.081080	0.065027
$p_4(4)$	0.191499	0.137879	0.103954	0.081224	0.065169
$p_4(5)$	0.190698	0.133704	0.103586	0.080914	0.064913
$p_4(6)$	0.191284	0.137771	0.103684	0.080994	0.065161
$p_4(7)$	0.191308	0.137730	0.103882	0.081134	0.065114
$p_4(8)$	0.19146	0.13780	0.10390	0.08113	0.06509

Table 8. The virial theorem $V/T = -\left(\frac{< P.E. >}{< K.E. >} \right)$ corresponding to the wavefunctions I to VIII for the two-electrons.

	H^-	He	Li^+	Be^{2+}	
	1	2	3	4	
$V/T(1)$	1.99804	1.99787	1.99898	1.99737	2.00078
$V/T(2)$	2.00187	1.99774	1.99927	1.99970	1.99974
$V/T(3)$	1.99867	2.00002	1.99990	1.99848	1.9989
$V/T(4)$	1.99981	1.99978	1.99954	2.00015	2.00007
$V/T(5)$	1.99873	1.99959	2.00242	1.99864	1.99871
$V/T(6)$	1.99855	1.99992	2.00044	2.00073	1.99959
$V/T(7)$	1.99921	2.00047	2.00007	1.99996	1.99984
$V/T(8)$	1.99970	2.00002	2.00001	2.00000	2.00000
	C^{4+}	N^{5+}	O^{6+}	F^{7+}	Ne^{8+}
	6	7	8	9	10
$V/T(1)$	2.00066	1.99920	1.99919	1.99927	1.99991
$V/T(2)$	1.99965	1.99968	1.99980	1.99984	1.99983
$V/T(3)$	1.99759	1.99897	1.99954	2.00029	1.99968
$V/T(4)$	2.00004	2.00010	1.99984	2.00017	2.00005
$V/T(5)$	1.99909	1.99913	1.99932	1.99942	1.99992
$V/T(6)$	2.00032	2.00091	1.99954	1.99980	2.00008
$V/T(7)$	1.99996	2.00005	2.00006	1.99998	1.99991
$V/T(8)$	2.00000	2.00000	2.00000	2.00000	1.99999

Table 9. The magnetic susceptibility (in cm^3) corresponding to the wavefunctions I to VIII for the two-electron systems.

	H^-	He	Li^+	Be^{2+}	B^{3+}
Z	1	2	3	4	5
$-\chi(1)$	16.169×10^6	1.840×10^6	0.694×10^6	0.361×10^6	0.222×10^6
$-\chi(2)$	17.093×10^6	1.881×10^6	0.702×10^6	0.366×10^6	0.224×10^6
$-\chi(3)$	17.121×10^6	1.876×10^6	0.706×10^6	0.366×10^6	0.224×10^6
$-\chi(4)$	16.820×10^6	1.899×10^6	0.709×10^6	0.368×10^6	0.225×10^6
$-\chi(5)$	16.796×10^6	1.897×10^6	0.708×10^6	0.366×10^6	0.224×10^6
$-\chi(6)$	16.846×10^6	1.890×10^6	0.708×10^6	0.367×10^6	0.224×10^6
$-\chi(7)$	16.652×10^6	1.867×10^6	0.702×10^6	0.366×10^6	0.224×10^6
$-\chi(8)$	15.780×10^6	1.889×10^6	0.707×10^6	0.367×10^6	0.225×10^6

	C^{4+}	N^{5+}	O^{6+}	F^{7+}	Ne^{8+}
Z	6	7	8	9	10
$-\chi(1)$	0.150×10^6	0.108×10^6	0.082×10^6	0.064×10^6	0.051×10^6
$-\chi(2)$	0.151×10^6	0.109×10^6	0.082×10^6	0.063×10^6	0.051×10^6
$-\chi(3)$	0.151×10^6	0.109×10^6	0.082×10^6	0.064×10^6	0.051×10^6
$-\chi(4)$	0.152×10^6	0.109×10^6	0.082×10^6	0.064×10^6	0.052×10^6
$-\chi(5)$	0.151×10^6	0.106×10^6	0.082×10^6	0.064×10^6	0.051×10^6
$-\chi(6)$	0.151×10^6	0.109×10^6	0.082×10^6	0.064×10^6	0.052×10^6
$-\chi(7)$	0.151×10^6	0.109×10^6	0.082×10^6	0.064×10^6	0.052×10^6
$-\chi(8)$	0.152×10^6	0.109×10^6	0.082×10^6	0.064×10^6	0.052×10^6

numerically. This fact confirms our assertion that the energy becomes better and better with the extension of the wavefunction in the configuration space. Further the inverse correlation function VIII with only 11 terms in its expansion yields an energy quite close to the 'exact' value. Moreover it appears from the tables that the simple two-term wavefunction VII having inverse correlation is also fairly accurate.

4. Conclusion

Our present calculation exhibits the importance of considering the physical properties while constructing the wavefunctions of the two-electron systems. These properties should be incorporated mathematically in the wavefunctions for proper description of the two-electron systems. Another interesting result of our finding is that (as is well known from earlier calculations [2,3,8,11,12]) the correlation function should fill up the entire configuration space in order to obtain the essentially 'exact' wave function. Finally, due to the simplicity and small size, our correlated wavefunctions can be used easily in further calculation of atomic and molecular physics where correlation dominates the desired result.

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